NANOPOROUS CARBONS DERIVED FROM BLOCK COPOLYMERS WITH POLYACRYLONITRILE BLOCKS

Chuanbing Tang, Michal Kruk, Krzysztof Matyjaszewski, Tomasz Kowalewski

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Ewa B. Celer, Mietek Jaroniec

Department of Chemistry, Kent State University, Kent, Ohio 44242

Keywords: polyacrylonitrile, block copolymer, nanoporous, atomic force microscopy

Abstract

Novel nanocarbons were synthesized from well-defined phase-separated polyacrylonitrile-poly(n-butyl acrylate) (PAN-b-PBA) diblock copolymers by pyrolysis, during which PAN domains were converted into carbon with concomitant decomposition of the PBA phase. The nanostructure of most of these materials resembled the morphology of their block copolymer precursors. Therefore, this new pathway allows for a control over nanocarbon architecture through a simple manipulation of block copolymer structure, including its composition and molecular weight. A variety of nanoscale morphologies, such as carbon (hemi)spheres, cylinders and lamellae were prepared using this route. Remarkably, this pathway opens an excellent chance to prepare thin or thick-film based carbons, which are usually difficult to be obtained by other methods, including the use of silica templates. The block copolymer precursors and corresponding nanostructured carbons were characterized by a variety of techniques, including atomic force microscopy, differential scanning calorimetry, thermogravimetry, transmission electron microscopy (TEM), X-ray diffraction, and Raman spectroscopy. Thermal behavior of PAN and PBA segments was thoroughly investigated and clarified. The carbons derived from PAN-b-PBA copolymers exhibit a certain degree of stacking of graphene sheets into semi-graphitic domains, but the degree of perfection of these structures is low. Further studies indicate that these carbon materials display nanoporosity in both bulk and film states, as determined by TEM and nitrogen adsorption. Our study of these materials is one of the earliest reports on the preparation of nanoporous carbons from block copolymers and our approach appears to be very convenient and attractive in applications requiring well-defined nanostructured carbon films.

REFERENCES

- 1. Kowalewski, T., Tsarevsky, N. V. and Matyjaszewski, K., "Nanostructured carbon arrays from block copolymers of polyacrylonitrile", *J. Am. Chem. Soc.*, 124, 36, 10632-10633 (2002).
- 2. Tang, C., Qi, K., Wooley, K., Matyjaszewski, K. and Kowalewski, T., "Well-defined Carbon Nanoparticles Prepared from Water Soluble Shell Cross-linked Micelles Containing Polyacrylonitrile Cores", *Angew. Chem. Int. Ed.*, 43, 2783-2787 (2004).
- 3. Tang, C., Kowalewski, T. and Matyjaszewski, K., "Preparation of Polyacrylonitrile-block-Poly(n-butyl acrylate) Copolymers Using Atom Transfer Radical Polymerization and Nitroxide Mediated Polymerization Processes", *Macromolecules*, 36, 5, 1465-1473 (2003).